On the High-Yielding Chlorodediazoniation not requiring Catalysis by Copper Salts

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Reaction of benzenediazonium tetrafluoroborate, *p*-methoxybenzenediazonium tetrafluoroborate, *p*-ethoxycarbonylbenzenediazonium tetrafluoroborate and 3-pyridinediazonium tetrafluoroborate in a 3:1 mixture of tetrachloromethane and acetonitrile with ferrous and ferric chloride yields the corresponding aryl chlorides in nearly quantitative yield. The reaction mechanism seems to be similar to that of the classical Sandmeyer reaction involving an initial electron transfer from the reductant to the arenediazonium ion. On the other hand, treatment of 2-aminopyridine or 2-amino-4-methylpyridine with dinitrogen trioxide in dry dichloromethane in the presence of hydrogen chloride and tetrabutylammonium chloride but in the absence of reducing agents afforded 2-chloropyridine or 2-chloro-4-methylpyridine, respectively, in 95 % yield in a reaction which either has a cation as intermediate or follows an S_NAr mechanism. The reactivity of the diazonium ion seems to determine whether the chlorodediazoniation goes through an aryl radical or follows another route, possibly via the S_NAr mechanism or the cation; most arenediazonium ions seem to react through the aryl radical, while 2-pyridinediazonium and most alkyldiazonium ions react via other routes.

A synthetically useful method for replacing an aromatic diazonium group with chloride or bromide was first described by Sandmeyer.[1] The mechanism of the reaction and the role of the copper salts in the reaction have been discussed for many years; a recent review[2] includes a historical account of the different viewpoints. It is, however, now generally accepted that the copper-catalysed chlorodediazoniation involves a two-step reaction as suggested by Waters[3] and Kochi[4] in which the Cu(I) complex transfers an electron to the diazonium compound with rapid loss of nitrogen, and the cupric chloride donates a chlorine atom to the aryl radical thus formed [eqns. (1) and (2)].

$$ArN_2^+ + CuCl_2^- \rightarrow Ar^\bullet + N_2 + CuCl_2 \quad (1)$$

$$Ar^\bullet + CuCl_2 \rightarrow ArCl + [CuCl] \quad (2)$$

$$Cl^- + [CuCl] \rightarrow CuCl_2^- \quad (3)$$

The cuprous chloride thus acts as a catalyst, and a low concentration of it should suffice; however, the highest yields are generally obtained when equimolar amounts of both cuprous and cupric chloride are present. The reason is that the diazonium compound may also react in other ways and the Sandmeyer reaction competes better with side reactions when both copper chlorides are present in concentrations similar to that of the diazonium salt.

The first reaction, the electron transfer to the diazonium salt, has been investigated in several ways. The polarographic half-wave potentials of a number of arenediazonium compounds have been measured in aqueous media[5,6] and in sulfolane[7] or DMF[8] and the potentials related to Hammett σ-values of the substituents in the aryl group.[7] The reduction is irreversible in cyclic voltammetry owing to the fast cleavage reaction after the uptake of an electron, and as the rate of the cleavage is not known and adsorption of the diazonium ion and/or the aryl radical to the electrode occurs, the thermodynamic significance of the polarographic and voltammetric potentials is uncertain. The electron transfer from hexacyanoferrate(II)[9] or hydroquinone monoanion[10] in aqueous phosphate buffer and from decamethylferrocene in acetonitrile[9] to a number of arenediazonium salts has been investigated by means of the stopped-flow technique, from which it was claimed that the reaction was an outer-sphere electron transfer.[9,10] The effect of the substituents on the aryl group, especially on the rate of the self-exchange reaction of the diazonium compounds, was, however, very much larger than is usual for an outer-sphere electron transfer; possibly the use of the polarographic half-wave potentials rather than the thermodynamic $E°$ is responsible for the unusual dependence of the rate of the self-exchange on substitution. The efficiency of different metal salts and other reducing agents on the chlorodediazoniation has been studied and a linear relationship between the reduction potential of the reducing agent and the yield of aryl chloride was observed. It was found that, in aqueous solution, ferrous chloride was not as effective a reducing agent as cuprous chloride.[11]

The aryl radical formed in reaction (1) may react in many ways: it may abstract a hydrogen atom from a suitable

donor with formation of ArH, it may dimerize to a biaryl, it can add to an unsaturated molecule, and it may abstract a halogen atom from a donor. Apart from the side reactions possible for the aryl radical, the arenediazonium salt may also decompose heterolytically to an aryl cation which reacts further. Cupric chloride is an excellent donor of chlorine atoms, but other donors may be used such as ferric chloride.[11] Titanium(III) chloride has been used both as a reducing agent in the reaction with diphenyliodonium chloride and as a chlorinating agent of the phenyl radical formed in the reduction,[12] and tetrachloromethane has been found[13] to react with phenyl radicals, obtained by thermal decomposition of phenylazotriphenylmethane, with a rate constant of about 3×10^6 M^{-1} s^{-1}.

In our current investigation on electron transfer in organic reactions we have studied the Sandmeyer reaction, and part of the work has been devoted to finding conditions which would give a high yield of product but which would not require the use of copper salts. The model reactions used are the transformation of substituted anilines into the corresponding chlorobenzenes and of aminopyridines into chloropyridines.

Results

In order to keep the heterolytic cleavage of the diazonium salts to a minimum, a relatively non-polar medium would be preferable; tetrachloromethane would have many advantages being both non-polar and a good chlorine-atom donor. The diazonium salts are, however, only sparingly soluble in this solvent, so acetonitrile (MeCN) was chosen as a co-solvent, even though an arylation of MeCN to acetanilide was a possible side reaction. Solubilization of the arenediazonium salt in CCl_4 using crown ethers[14] or poly(ethyleneglycol)[15] might be another possibility.

Several reducing agents were tried, namely ferrocene, ferrous chloride, ferrous sulfate, stannous chloride, and ascorbic acid. Ferrous sulfate and ascorbic acid were too insoluble in acetonitrile and stannous chloride gave only very low yields in preliminary experiments, so further work with these reductants was discontinued.

Ferrocene was chosen as a reductant which could deliver an electron, but not act as a chlorinating agent. Ferrocene reacted rapidly with benzenediazonium tetrafluoroborate (**1**) in a MeCN/CCl_4 mixture, as indicated by the immediate appearance of the blue colour of the ferrocenium ion. On reaction of ferrocene with **1** in MeCN/CCl_4, chlorobenzene (**2**) was the main product with phenylferrocene and hexachloroethane as by-products. The results given in Table 1 show that the yields of **2** were not satisfactory, the highest yield being 70%. The highest yields of **2** were obtained when a medium consisting of 1:3 v/v MeCN/CCl_4 (medium A) was used. Relatively small concentrations of the reactants, which decrease the rate of reaction between the phenyl radical and ferrocene/ferrocenium, also seem to favour the formation of **2**. However, the competition for the aryl radical between tetrachloromethane and ferrocene is strong, and relatively small changes in reaction conditions alter the product distribution. In some cases very small amounts of by-products such as acetanilide, biphenyl, chlorobiphenyl and azobenzene could be detected by GLC–MS.

Another possible reductant is ferrous chloride. In aqueous solution ferrous ions are not sufficiently reducing,[11] so the system ferrous/ferric chloride is, under such conditions, rather inefficient for promoting the chlorodediazoniation. However, in a medium consisting of a mixture MeCN/CCl_4, ferrous chloride is an effective reductant, and under suitable conditions the yield of chlorodediazoniation is nearly quantitative (Table 2). It is, however, remarkable that it is dissolving ferrous chloride that is effective as the reductant, ferrous ions solvated by MeCN react slowly, if at all.

The best yields of **2** were obtained in medium A; at higher concentrations of MeCN side reactions become significant, and at higher CCl_4 concentrations the yield of **2** again drops, possibly because the diazonium salt is too insoluble and the dissolution of ferrous chloride becomes slower. Among the side products detected were acetani-

Table 1. Concentration of ferrocene and PhN_2^+, solvent composition (volume ratio; V_{MeCN}/V_{CCl_4}), and yield of chlorobenzene (**2**) and phenylferrocene. The total volume of the solvent is between 6 and 45 ml and the uncertainty in the determination of yield is ± 5%.

$C_{Ferrocene}$/M	$C_{PhN_2^+BF_4^-}$/M	$V_{CH_3CN}:V_{CCl_4}$	**2** (%)	Phenylferrocene (%)
0.65	0.21	1:4	12	50
0.54	0.17	1:2	42	34
0.54	0.17	1:1	41	27
0.36	0.17	1:2	38	26
0.18	0.17	1:2	35	24
0.18	0.17	1:3	43	26
0.18	0.07	1:2	60	17
0.18	0.07	1:3	59	17
0.067	0.058	1:8	26	23
0.067	0.026	1:1	62	12
0.027	0.026	1:2	56	6
0.027	0.026	1:3	70	4
0.013	0.013	1:4	52	1

Table 2. Concentration of $FeCl_2$, $FeCl_3$ and PhN_2^+, solvent composition (volume ratio; V_{MeCN}/V_{CCl_4}),[a] and yield of chlorobenzene (**2**). The uncertainty in the determination of the yield is ± 5 %.

C_{FeCl_2}/M	C_{FeCl_3}/M	$C_{PhN_2+BF_4^-}$/M	$V_{CH_3CN}:V_{CCl_4}$	**2** (%)
0	0.62	0.52	2:0	0
0	1.56	0.52	2:0	0
0.80	0	0.52	2:0	57
1.18	0.62	0.52	2:0	78
0.20	0	0.13	2:6	72
0.50	0	0.13	2:6	78
1.00	0	0.13	2:6	75
0.20	0.08	0.13	2:6	71
0.20	0.15	0.13	2:6	76
0.30	0.23	0.13	2:6	79
0.30	0.62	0.13	2:6	88
0.40	0.08	0.13	2:6	80
0.40	0.15	o.13	2:6	95
0.40	0.31	0.13	2:6	98
0.50	0.39	0.13	2:6	98

[a] $V_{MeCN}:V_{CCl_4}$ shows the volume in ml of the solvents used.

lide, biphenyl, chlorobiphenyl, azobenzene and hexachloroethane.

The presence of ferric chloride is also essential for a quantitative yield of product. Ferrous chloride in MeCN gives a 57 % yield of **2**, which was raised to nearly 80 % when CCl_4 was added (MeCN/CCl_4 = 1:3). A similar result is obtained if both ferrous and ferric chlorides are used in MeCN. Use of ferrocene as the reducing agent instead of ferrous chloride in the presence of ferric chloride in MeCN led to a 50 % yield of chlorobenzene, showing the ability of ferric chloride to act as a ligand-transfer agent. If ferric chloride but no reducing agent is present no chlorobenzene is formed. The highest yield (ca. 98 %) of chlorobenzene from benzenediazonium tetrafluoroborate was obtained in a medium A when both ferrous and ferric chlorides are present in concentrations at least equivalent to the diazonium salt. Ambient temperature was used.

Under the same conditions the three diazonium compounds *p*-methoxybenzenediazonium tetrafluoroborate, *p*-ethoxycarbonylbenzenediazonium tetrafluoroborate and 3-pyridinediazonium tetrafluoroborate were all converted into the corresponding aryl chlorides in at least 95 % yield. Even though the electron-donating methoxy group lowers the reduction potential of the diazonium salt and thus the rate of the electron transfer, the yield of the corresponding chloride is not diminished. Even the use of a heteroaromatic system such as the 3-pyridinediazonium salt does not decrease the efficiency of the method described; the yield is still almost quantitative.

The Sandmeyer reaction of 2-aminopyridine (**3**) to 2-chloropyridine (**4**) using the usual conditions gives little or no **4**;[16] nitrosation of 2-aminopyridine in 0.0025–5 M perchloric acid has been found to be reversible.[17] The reaction performed in concentrated hydrochloric acid is reported to give a quantitative yield of **4**;[16] however, in our hands, the yield of **4** never exceeded 70 %. Reaction of **3** in MeCN with *t*-butyl thionitrite or *t*-butyl thionitrate in the presence of cupric chloride afforded **4** in 35 and 64 % yield, respectively.[18] In order to establish whether the dediazoniation proceeded through a cation or through a radical, diazotization was performed in non-aqueous solvents in a manner similar to that used for **1**.

2-Pyridinediazonium tetrafluoroborate and its 4-methyl analogue could not be precipitated from aqueous solution analogously to the other compounds, so the diazotization was therefore made *in situ* using N_2O_3 as the nitrosating agent. Attempts to use MeCN saturated with dry hydrogen chloride as the solvent gave a modest yield (20–30 %) of **4** (Table 3); the main by-products are 2-acetamidopyridine and 2-hydroxypyridine. Acetonitrile and water thus seem to be a problem. A number of solvent systems consisting of a mixture of a polar aprotic and a chlorinated solvent saturated with hydrogen chloride were used with improved results (yields 50–70 %), but since water is generated during the formation of the diazonium salt from the amine and N_2O_3, 2-hydroxypyridine is still produced in a significant yield. The use of the liquid electrolyte, butylpyridinium chloride/aluminium chloride in which water would be removed with $AlCl_3$ with formation of hydrogen chloride gave an acceptable yield of 2-chloropyridine (ca. 75 %). The melt is, however, cumbersome to prepare pure and not especially suitable as a solvent, but the result showed that it was possible to obtain fair-to-good yields of 2-chloropyri-

Table 3. The yield of 2-chloropyridine (**4**) in different solvent systems.

Solvent system	**4** (%)
CH_3CN	20–30
CH_2Cl_2, CH_3NO_2 and similar solvents	50–70
$AlCl_3$–butylpyridinium chloride	75
CH_2Cl_2 with $AlCl_3$	80
CH_2Cl_2 with TBACl	95

dine under almost non-aqueous conditions. The treatment of 2-aminopyridine with dinitrogen trioxide in dry dichloromethane in the presence of dry hydrogen chloride and anhydrous aluminium chloride also afforded 2-chloropyridine in good yield (80 %).

The use of tetrabutylammonium chloride (TBACl) in the dichloromethane solution instead of aluminium chloride increased the yield to 95 %. The concentration of TBACl does not need to be equivalent to that of 2-aminopyridine; chloride ion from hydrogen chloride may also contribute. Under these conditions 2-amino-4-methylpyridine was also converted into the corresponding chloride in nearly quantitative yield. It is remarkable, however, that chloride ion in the medium reacts less efficently in the absence of TBACl. The reactions were run at ambient temperature and protected from moisture; slightly elevated temperatures (ca. 35 °C) gave similar yields in a somewhat faster reaction.

Discussion

In the reaction between ferrocene and benzenediazonium ion the main products were chlorobenzene, hexachloroethane and phenylferrocene. In some cases small amounts of by-products were detected. The main by-product (a few per cent) was acetanilide. The reactions can be formulated as shown in eqns. (4)–(9). An attack by phenyl radical on

$$C_{10}H_{10}Fe + C_6H_5N_2^+ \rightarrow C_{10}H_{10}Fe^+ + C_6H_5^{\cdot} + N_2 \quad (4)$$

$$C_6H_5^{\cdot} + CCl_4 \rightarrow C_6H_5Cl + CCl_3^{\cdot} (\rightarrow Cl_3CCCl_3) \quad (5)$$

$$C_{10}H_{10}Fe^+ + C_6H_5^{\cdot} \rightarrow C_6H_5\text{–}C_{10}H_9Fe + H^+ \quad (6)$$

$$C_6H_5^{\cdot} + CH_3CN + (H_2O) \rightarrow\rightarrow C_6H_5NHCOCH_3 \quad (7)$$

$$C_6H_5N_2^+ \rightarrow C_6H_5^+ + N_2 \quad (8)$$

$$C_6H_5^+ + CH_3CN + (H_2O) \rightarrow\rightarrow C_6H_5NHCOCH_3 + H^+ \quad (9)$$

ferrocenium is shown in reaction (6), but it is not actually known whether phenylferrocene is formed by attack of the phenyl radical on ferrocene or on ferrocenium. Some (or all) of the acetanilide might be formed after heterolytic cleavage of benzenediazonium tetrafluoroborate [eqns. (8), (9)] rather than by radical attack [eqn. (7)]; in some of the experiments no acetanilide was detected by GLC. When benzenediazonium tetrafluoroborate is dissolved in MeCN in the absence of any reducing agents at 20 °C a fair yield of acetanilide is obtained after some hours. Furthermore, electrochemical reduction of benzenediazonium tetrafluoroborate carried out with a platinum plate electrode or a mercury pool in acetonitrile/0.1 M tetrabutylammonium tetrafluoroborate gave only traces of acetanilide, indicating that the electrochemically generated phenyl radicals did not react with acetonitrile. The reduction was performed at 0 °C in order to diminish the heterolytic cleavage of the diazonium compound.

The reaction of benzenediazonium ion in a mixture of acetonitrile and tetrachloromethane did not produce any chlorobenzene in the absence of ferrous chloride, whereas, in the presence of both ferrous and ferric chloride, it afforded **2** in nearly quantitative yield. These findings point to a reaction mechanism similar to that of the classical Sandmeyer reaction,[3,4] according to which, ferrous chloride would reduce the diazonium ion to dinitrogen and phenyl radical, while ferric chloride and tetrachloromethane would function as chloride-atom donors.

$$C_6H_5N_2^+BF_4^- + FeCl_2 \rightarrow C_6H_5^{\cdot} + FeCl_2BF_4 + N_2 \quad (10)$$

$$C_6H_5^{\cdot} + FeCl_3 \rightarrow C_6H_5Cl + FeCl_2 \quad (11)$$

$$C_6H_5^{\cdot} + FeCl_2BF_4 \rightarrow C_6H_5Cl + FeClBF_4 \quad (12)$$

$$C_6H_5^{\cdot} + CCl_4 \rightarrow C_6H_5Cl + CCl_3^{\cdot} \quad (13)$$

This is in accordance with the finding that the one-electron reductant ferrocene was able to bring about the dediazoniation. It is also noteworthy that ferrous chloride, in the absence of ferric chloride, in acetonitrile with no tetrachloromethane affords a fair yield of chlorobenzene (50 %). Thus the ferric salt formed from ferrous chloride after the transfer of an electron can act as a ligand-transfer agent [eqn. (12)]. The role of the ferrous chloride is thus exactly the same as that of cuprous chloride in the conventional Sandmeyer reaction. In principle, a small amount of ferrous chloride should be sufficient to give a reasonable yield of **2**, but in practice the yield under such conditions is very low.

It is interesting that ferrous chloride solvated by acetonitrile is not effective as a reductant, the reduction requiring the presence of solid ferrous chloride. This phenomenon may also explain why the reaction cannot be performed with ferrous chloride in catalytic amount, since this would be dissolved and solvated immediately. The solvation (complexation) of ferrous ions by acetonitrile probably raises the oxidation potential of the ferrous ion as compared with the uncomplexed ferrous ion with the result that it becomes too poor a reductant to reduce the diazonium ion at a sufficiently high rate. This is in accordance with the finding[11] that ferrous ion in aqueous solution is inefficient as a reducing agent toward benzenediazonium ions.

The reaction of 2-pyridinediazonium ion seems to follow a different route. Ferrous ions or other reducing agents are not necessary and seem to have no effect on the reaction. This is probably because of the reactivity of the protonated 2-pyridinediazonium ion and the high reactivity of the cation formed on loss of dinitrogen. The cation would react with any nucleophile, including water or the solvent (CH_3CN), which also points to the intermediacy of the cation rather than the pyridyl radical. The reactions can be formulated as shown in eqns. (14)–(17).

$$H^+NC_5H_4N_2^+ \rightarrow (NC_5H_4)^+ + N_2 + H^+ \quad (14)$$

$$(NC_4H_4)^+ + Cl^- \rightarrow NC_5H_4Cl \quad (15)$$

$$(NC_5H_4)^+ + H_2O \rightarrow HNC_5H_4O + H^+ \quad (16)$$

$$(NC_5H_4)^+ + CH_3CN \rightarrow NC_5H_4\overset{+}{N}{\equiv}CCH_3 \xrightarrow{H_2O} HN^+C_5H_4NHCOCH_3 \quad (17)$$

It is somewhat surprising that the reaction apparently goes via the cation rather than via the radical; the reduction potential of the protonated pyridinediazonium ion would be expected to be rather positive, some hundred mV more positive than that of the benzenediazonium ion, if the difference in the pK_A values of (protonated) picolinic acid ($pK_A = 1.01$)[19] and benzoic acid ($pK_A = 4.19$) can be used to estimate the σ-value of the species and if the reduction potential of the 2-pyridinediazonium salt follows the Hammett equation in the same way as shown for a number of arenediazonium salts.[7] However, even if the reduction potential of the protonated pyridinediazonium ion is some hundred mV more positive than that of benzenediazonium ion it seems unlikely that chloride ion would act as an electron donor toward the pyridinediazonium ion. The cation must be a high energy species, although the positive charge may be on the nitrogen thus forming a hetaryne. A direct attack by the nucleophile on the protonated pyridinediazonium ion in an S_NAr reaction may also be a possibility.[20]

The results indicate that the reaction mechanism of the dediazoniation in the presence of a suitable reductant depends on the reactivity of the diazonium ion. When it is relatively stable, as found for most arenediazonium compounds, the second-order reaction, the electron transfer from a reductant, can compete with the first-order heterolytic cleavage of the diazonium ion, whereas more reactive diazonium ions react *via* a loss of dinitrogen to form a cation or *via* an S_NAr mechanism even in the presence of a good reductant. Examples of such diazonium ions are the derivatives of 2-pyridinediazonium and most aliphatic diazonium ions. It is to be expected that in a certain region of stability of the diazonium ion, changes in reaction conditions (concentration, temperature, reducing agent) may significantly influence the competition between the different reaction routes.

Experimental

Apparatus. The ^1H NMR spectra were recorded with a Varian Gemini 200 MHz spectrometer. GLC was performed with a Hewlett-Packard 5890 gas chromatograph with an OV-101 Column: injector temperature 250 °C; 80 °C for 5 min to 250 °C at 8 °C min^{-1}. Naphthalene and anisole were used as internal standards. For the GLC–MS analyses a Hewlett-Packard 5890 gas chromatograph combined with a VG Masslab mass spectrometer was used.

Materials. Chlorobenzene, 4-chloroanisole, 2-aminopyridine, 2-chloro-4-methylpyridine, 3-chloropyridine, hexachloroethane, tetrabutylammonium chloride, aluminium chloride, ferric chloride and ferrocene were obtained commercially. Ethyl 4-chlorobenzoate was prepared through the diazonium compound using the method presented in this paper and purified before use through a silica-gel column with methylene chloride as the eluent. Phenylferrocene was prepared by reacting an excess of ferrocene with benzenediazonium tetrafluoroborate in methylene chloride. It was separated from the excess of ferrocene on a preparative plate of silica with 8 % chloroform–light petroleum as the eluent. Acetonitrile (MeCN) was purified by standard procedures.

Benzenediazonium tetrafluoroborate,[21] *p*-methoxybenzenediazonium tetrafluoroborate,[22] *p*-ethoxycarbonylbenzenediazonium tetrafluoroborate,[23] 3-pyridinediazonium tetrafluoroborate,[22] 2-amino-4-methylpyridine,[24] and the salt $AlCl_3$–butylpyridinium chloride[25] were prepared according to the references given.

Ferrous chloride, $FeCl_2$, was prepared from commercial $FeCl_2 \cdot 6H_2O$. 20 g of $FeCl_2 \cdot 6H_2O$, 15 g of iron powder, and 100 ml of 4 M hydrochloric acid were placed in a 200 ml flask. The role of the iron was to reduce impurities of iron(III) to iron(II). The solution was stirred and heated to 80 °C for 2 h during which the colour of the solution changed from brown to green. Afterwards the HCl solution was filtered to remove unchanged iron and the filtrate was evaporated carefully to dryness to prevent oxidation of ferrous chloride. The yellow–green ferrous chloride was dried in air before use; it did not change colour for several weeks, even when no special precautions were made to exclude air from the container.

Determination of yield. The determination of yields was mostly performed by means of GLC using naphthalene and anisole as internal standards. In the experiments where a nearly quantitative yield was found by GLC the results were verified by isolation of the product.

Reaction of $PhN_2^+BF_4^-$ (1) with $FeCl_2$ and $FeCl_3$. A typical experiment was performed as follows. Benzenediazonium tetrafluoroborate (**1**, 0.20 g, 1.04 mmol) was dissolved in a mixture of 6 ml CCl_4 and 2 ml MeCN (medium A). To this solution was added a mixture of $FeCl_2$ (0.40 g, 3.16 mmol) and $FeCl_3$ (0.20 g, 1.23 mmol) with stirring. Nitrogen was formed and a few minutes later the reaction was complete. The yield of chlorobenzene was 95 %.

Reaction of **1** *with ferrocene.* The procedure was almost the same except that no $FeCl_3$ was added and a larger volume of the solvent mixture was generally used (6–45 ml) in order to decrease the concentrations of the reactants and thus the rate of formation of phenylferrocene. In a typical example ferrocene (0.20 g, 1.08 mmol) was added to a solution of benzenediazonium tetrafluoroborate (**1**, 0.20 g, 1.04 mmol), which had been dissolved in a mixture of 30 ml

CCl_4 and 10 ml CH_3CN. Nitrogen evolved. The yield (GLC) of chlorobenzene was 70 % and of phenylferrocene 4 %. 25 mg of hexachloroethane were formed, corresponding to 27 % of the highest possible yield of hexachloroethane. In some of the reactions small amounts of by-products such as acetanilide, biphenyl, chlorobiphenyl and azobenzene were detected by GLC–MS.

Chlorobenzene [*m/z*(%)]: 114 (31), 112 (100), 77 (60), 51 (25), 50 (25). Phenylferrocene [*m/z*(%)]: 263 (23), 262 (100), 141 (27), 121 (31), 115 (29), 56 (31). Hexachloroethane [*m/z*(%)]: 204 (14), 203 (45), 201 (67), 199 (41), 168 (18), 166 (40), 164 (30), 117 (100), 94 (35), 82 (27), 47 (30). Acetanilide [*m/z*(%)]: 135 (30), 92 (100), 65 (25), 42 (30), 28 (52). Biphenyl [*m/z*(%)]: 154 (100), 127 (10), 76 (15), 62 (12), 51 (20). Chlorobiphenyl [*m/z*(%)]: 190 (32), 188 (100), 152 (80), 127 (20), 76 (15), 62 (10), 51 (20). Azobenzene [*m/z*(%)]: 182 (30), 152 (15), 127 (15), 105 (21), 77 (100), 51 (52).

Reaction of **1** (0.40 g, 2.08 mmol) with ferrocene (0.60 g, 3.23 mmol) in 8 ml of MeCN and $FeCl_3$ (0.40 g, 2.47 mmol) as a chlorine-atom donor afforded **2** in 50 % yield.

The conversion of *p*-methoxybenzenediazonium tetrafluoroborate, *p*-ethoxycarbonylbenzenediazonium tetrafluoroborate and 3-pyridinediazonium tetrafluoroborate into the corresponding chlorides by the use of $FeCl_2$ and $FeCl_3$ in medium A followed the same procedure described for **1**.

MS: *p*-Chloroanisole [*m/z*(%)]: 144 (36), 142 (100), 129 (20), 127 (62), 101 (21), 99 (65), 75 (20), 73 (20), 63 (22). 3-Chloropyridine [*m/z*(%)]: 115 (38), 113 (100), 78 (63), 51 (28), 50 (17).

^{1}H NMR for ethyl 4-chlorobenzoate: δ 1.37 (t, 3 H, J = 7.30 Hz), 4.35 (q, 2 H, J = 7.30 Hz), 7.38 (d, 2 H, J = 8.40 Hz), 7.95 (d, 2 H, J = 8.40 Hz).

Reaction of 2-aminopyridine with N_2O_3 and TBACl. 2-Aminopyridine (0.50 g, 5.31 mmol) and tetrabutylammonium chloride (1.00 g, 3.60 mmol) were dissolved in 50 ml of dry methylene chloride. Hydrogen chloride gas was bubbled through the solution for a few minutes to convert the amine almost completely into the salt. A stream of N_2O_3 was then passed through the solution with stirring. The N_2O_3 was produced in a 50 ml three-necked flask containing $NaNO_2$. Concentrated H_2SO_4 was added by means of a dropping funnel and the N_2O_3 formed was transferred to the reaction flask in a stream of nitrogen. Slow evolution of nitrogen ensued. When the solution became red–brown in colour the addition of N_2O_3 was stopped; if the colour faded more N_2O_3 was added. The reaction was complete within 2 h at room temperature; when heated to ca. 35 °C the reaction was faster. The yield of 2-chloropyridine was 95 %. MS [*m/z*(%)]: 115 (5), 113 (13), 78 (28), 62 (15), 52 (36), 51 (100), 50 (92).

In a similar way and with a similar yield 2-amino-4-methylpyridine was transformed into 2-chloro-4-methylpyridine. MS [*m/z*(%)]: 129 (31), 127 (100), 92 (85), 65 (45), 63 (13), 50 (9), 39 (21).

Reaction of 2-aminopyridine with N_2O_3 and $AlCl_3$. The procedure was the same that as described above, except that $AlCl_3$ (0.50 g, 3.75 mmol) was used instead of TBACl; yield of 2-chloropyridine about 80 %. When $AlCl_3$–butylpyridinium chloride was used as the solvent instead of dichloromethane, the yield of 2-chloropyridine was about 75 %. In order to obtain such a yield, effective stirring is necessary to maintain a homogeneous solution.

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